

ALUMINA VOLATILITY IN WATER VAPOR AT ELEVATED TEMPERATURES: APPLICATION TO COMBUSTION ENVIRONMENTS

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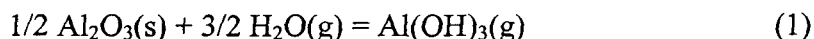
The volatility of alumina in high temperature water vapor was determined by measuring weight loss of sapphire coupons at temperatures between 1250 and 1500°C, water vapor partial pressures between 0.15 and 0.68 atm in oxygen, at one atmosphere total pressure, and a gas velocity of 4.4 cm/s. The variation of the volatility with water vapor partial pressure was consistent with $\text{Al}(\text{OH})_3(\text{g})$ formation. The enthalpy of reaction to form $\text{Al}(\text{OH})_3(\text{g})$ from alumina and water vapor was found to be 210 ± 20 kJ/mol. Surface rearrangement of ground sapphire surfaces increased with water vapor partial pressure, temperature and volatility rate. Recession rates of alumina due to volatility were determined as a function of water vapor partial pressure and temperature to evaluate limits for use of alumina in long term applications in combustion environments.

INTRODUCTION

Efficiency of turbine engines for both power generation and propulsion can be increased by raising the operation temperature of the engine. To attain these increased efficiencies, there is a need for higher temperature materials. Current goals are to find materials that can be used, uncooled, at temperatures between 1200 and 1650°C. Since water vapor is present in combustion environments [1], a material of choice for this application must be stable in water vapor at these elevated temperatures. Silica forming materials (silicon carbide and silicon nitride) have been considered for structural applications in combustion environments; however, it was found that the thermally grown silica scale reacts with water vapor to form volatile hydroxides in combustion environments, precluding use for long-term applications [2,3]. Alumina is considered to be a more stable oxide than silica under combustion conditions. It is being considered for use in combustion environments as a component of oxide/oxide composites [4] or as a constituent of high temperature coatings [5]. The stability of alumina in water vapor at elevated temperatures must therefore be assessed.

The primary reaction by which alumina forms a volatile hydroxide species in combustion environments is considered to be:

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The formation of this volatile species is predicted to dominate in combustion environments based on thermochemical data of Gurvich et al. [6]. Gurvich et al. estimated thermochemical data for $\text{Al}(\text{OH})_3(\text{g})$ based on the structure of similar molecules such as $\text{AlF}_3(\text{g})$ and $\text{B}(\text{OH})_3(\text{g})$. Calculation of the primary volatile species for Al_2O_3 in 1 bar H_2O /1 bar O_2 using the Gurvich data is shown in Figure 1. Other volatile species besides $\text{Al}(\text{OH})_3(\text{g})$ are not expected to become important until temperatures above 1800°C are achieved. Additional support for reaction 1 is based on the transpiration study of Hashimoto [7]. Hashimoto conducted experiments in which water vapor was carried over a mixture of $\text{CaAl}_4\text{O}_7(\text{s})$ and $\text{CaAl}_2\text{O}_4(\text{s})$ by flowing argon. Volatile hydroxide species were formed, condensed downstream, and quantified. Using known data for $\text{Ca}(\text{OH})_2(\text{g})$ formation, the volatility of alumina was determined. The alumina volatility was found to vary with water vapor partial pressure with a power law exponent of 3/2, consistent with reaction 1. Finally, Yuri et al. [8] measured and quantified Al_2O_3 recession in a combustion rig. The pressure and temperature dependence of recession by volatilization were also consistent with $\text{Al}(\text{OH})_3(\text{g})$ formation.

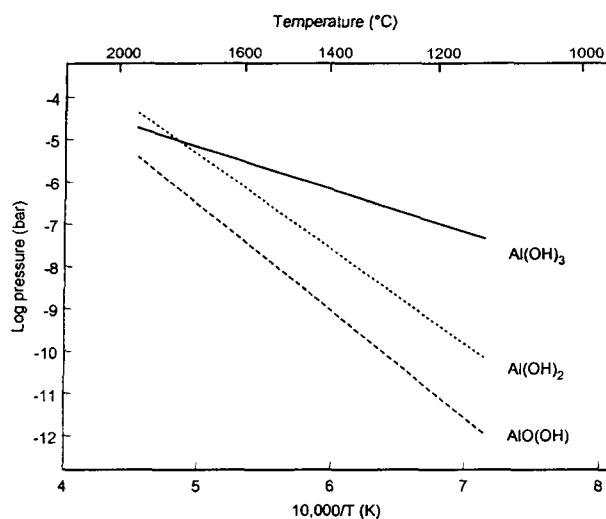


Figure 1. Volatile species in the Al-O-H system, calculated for $\text{Al}_2\text{O}_3 + 1 \text{ bar H}_2\text{O}(\text{g}) + 1 \text{ bar O}_2(\text{g})$ using the estimated data of Gurvich et al. [6].

The objectives of this work were to experimentally measure alumina volatility in water vapor directly from pure alumina, to determine the temperature and water vapor partial pressure dependence of alumina volatility, and to identify combustion conditions where alumina volatility limits useful component life.

EXPERIMENTAL PROCEDURE

Weight loss of sapphire coupons (0001) basal plane orientation, flame fusion grown, <100 ppm impurities (General Ruby and Sapphire Corporation, New Port Richey, FL) was determined. Coupons were 2.5 x 1.25 x 0.2 cm in size. Coupon volatilities were

measured in water vapor partial pressures varying between 0.15 and 0.68 atm, in oxygen, at 1 atm total pressure. Total gas velocities were equivalent to 4.4 cm/sec at room temperature (corresponding to 1000 ccm in a tube of inner diameter equal to 2.2 cm). Weight loss was determined at 50°C intervals between 1250 and 1500°C. Exposure times varied between 47 and 240 hours. Control experiments were also conducted in dry oxygen. The experimental setup has already been described [2].

Samples were suspended from sapphire hangers in a Cahn 1000 microbalance. Fused quartz reaction tubes were used because they are alumina-free and high purity. Condensation of volatile species on the hanger in the cooler part of the furnace prevented accurate determination of weight change by thermogravimetric analysis, therefore, the coupon weight change was determined from initial and final coupon weights measured with a bench top balance. However, the sample suspension method resulted in laminar flow over the flat plate coupon which enabled use of the kinetic model discussed below.

Sapphire coupons were examined by X-Ray Diffraction (XRD) and Field Emission Scanning Electron Microscopy (FE-SEM) after exposure.

KINETIC MODELING OF VOLATILIZATION RATE

The measured weight loss was used to calculate a partial pressure of volatile $\text{Al}(\text{OH})_3(\text{g})$ assuming the volatilization of alumina to form $\text{Al}(\text{OH})_3(\text{g})$ was limited by transport of this species outward through a gaseous laminar boundary layer. This relationship is given for a flat plate geometry by the following expression [9,10]:

$$\frac{\Delta w}{At} = 0.664 \text{Re}^{1/2} \text{Sc}^{1/3} \frac{DP_{\text{Al}(\text{OH})_3} M}{LRT} \quad [2]$$

where Δw is the measured weight change, A is the coupon surface area, t is the time, Re is the dimensionless Reynold's number, Sc is the dimensionless Schmidt number, D is the interdiffusion coefficient of $\text{Al}(\text{OH})_3$ in the boundary layer gas, $P_{\text{Al}(\text{OH})_3}$ is the partial pressure of the volatile $\text{Al}(\text{OH})_3$ to be calculated, M is the molecular weight of $\text{Al}(\text{OH})_3$, L is a characteristic length of the coupon, R is the gas constant, and T is the absolute temperature. All gases are assumed ideal. This equation can be further expanded:

$$\frac{\Delta w}{At} = 0.664 \left(\frac{Lvp}{\eta} \right)^{1/2} \left(\frac{\eta}{\rho D} \right)^{1/3} \frac{DP_{\text{Al}(\text{OH})_3} M}{LRT} \quad [3]$$

where v is the gas velocity, η is the gas viscosity, and ρ is the concentration of the boundary layer gas. The interdiffusion coefficient was calculated using the Chapman Enskog Equation [11] with collision integrals and collision diameters of AlF_3 [12] as estimates for $\text{Al}(\text{OH})_3$. Equation 3 was used to determine the partial pressure of $\text{Al}(\text{OH})_3(\text{g})$ from the experimentally measured weight changes of the sapphire coupons.

This expression was simplified to the combustion environment parameters of pressure, velocity, and temperature:

$$\frac{\Delta w}{A t} \propto \frac{v^{1/2} P_{\text{Al(OH)}_3}}{P_{\text{total}}^{1/2}} \quad [4]$$

where, here $P_{\text{Al(OH)}_3}$ is distinguished from the total pressure, P_{total} , of the boundary layer gas. The pressure dependence of P_{total} arises from the combined pressure dependence of $\rho \propto P$ and $D \propto 1/P$. The temperature dependence of the weight change is contained in the $P_{\text{Al(OH)}_3}$ term, is exponential, and arises from the heat of formation of $\text{Al(OH)}_3(\text{g})$ by Reaction 1. The temperature dependence is dominated by the $P_{\text{Al(OH)}_3}$ term, therefore, the temperature dependencies of D , η , and ρ have been neglected. Also, knowing that $P(\text{Al(OH)}_3)$ is proportional to $P(\text{H}_2\text{O})^{3/2}$ from Reaction 1, and $P(\text{H}_2\text{O})$ is equal to about $0.1 P_{\text{total}}$ as discussed earlier, then:

$$\frac{\Delta w}{A t} \propto v^{1/2} P_{\text{total}} \exp\left(\frac{-\Delta H_{\text{rxn}}}{RT}\right) \quad [5]$$

Equation 5 was used to determine the enthalpy of formation of Reaction 1 as well as to map out application limits for alumina in combustion environments as a function of temperature and pressure.

RESULTS AND DISCUSSION

The linear weight loss rates of sapphire coupons, k_1 , which are synonymous with $\Delta w/A t$, are plotted in Figure 2 as a function of temperature. These rates vary between 3×10^{-4} and $4 \times 10^{-3} \text{ mg/cm}^2 \text{ h}$ in the temperature range studied here. This plot is included so that the volatility of sapphire can be extrapolated in terms of weight loss using Equation 5. The temperature range was limited at the low end by extremely low weight loss rates. For example, a 240h exposure in 50% $\text{H}_2\text{O}/50\% \text{ O}_2$ at 1250°C resulted in only 0.8 mg weight loss. The experiments were limited at the high end of the temperature range by mullite formation. Volatile Si-O-H species were carried from the fused quartz tube to the sapphire coupon surface where mullite was nucleated. After exposure, each coupon was analyzed by XRD to look for mullite formation. Mullite was not observed at exposure temperatures below 1500°C . Two of the three coupons exposed at 1500°C showed surface mullite formation. However, the weight loss results were not significantly different from the coupon which did not exhibit surface mullite formation, suggesting the weight gain due to mullite formation under these conditions was negligible.

The data are replotted in terms of partial pressure in Figure 3. These results, as well as the pressure dependence are published elsewhere [13], but are included here for completeness. The partial pressures of $\text{Al(OH)}_3(\text{g})$ under the conditions studied here vary between 5×10^{-8} and $8 \times 10^{-7} \text{ atm}$. The enthalpy of Reaction 1 was determined from this plot and was found to be $210 \pm 20 \text{ kJ/mol}$. Both the magnitude of the partial pressure of volatile $\text{Al(OH)}_3(\text{g})$ and the temperature dependence are in good agreement with the results based on estimated thermochemical data of Gurvich [6] and the experimental transpiration results from the Ca-Al-O-H system by Hashimoto [7]. This is good agreement considering the assumptions made in applying the model of volatility limited

by transport through a gaseous boundary layer for laminar flow over a flat plate given by Equation 3.

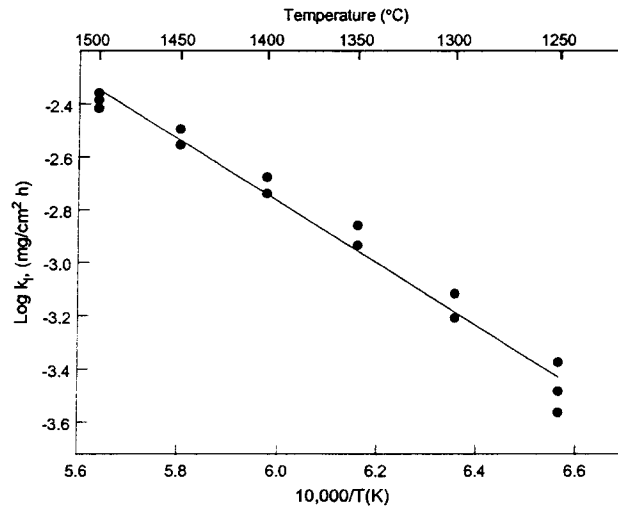


Figure 2.
Experimentally measured weight loss rates for Al_2O_3 in 0.5 atm H_2O /0.5 atm O_2 .

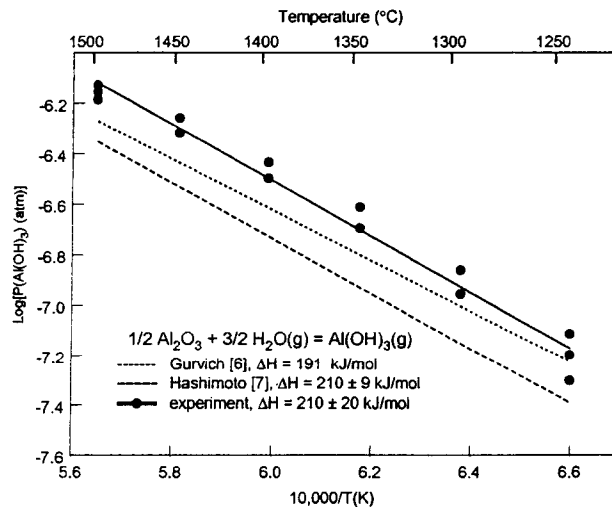


Figure 3. Measured temperature dependence of $\text{Al(OH)}_3(\text{g})$ formation in 0.5 atm H_2O /0.5 atm O_2 . Results are compared to the literature.

The water vapor partial pressure dependence of the sapphire coupon volatility is shown in Figure 4. A slope of 1.5 is predicted for $\text{Al(OH)}_3(\text{g})$ formation based on Reaction 1. The experimental value obtained was 1.55 ± 0.11 which is consistent with $\text{Al(OH)}_3(\text{g})$ formation.

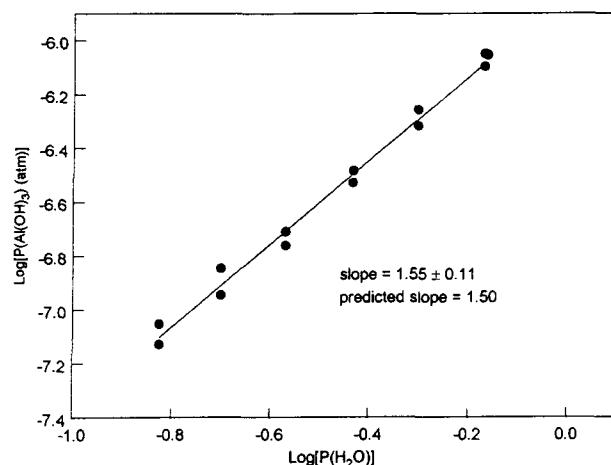


Figure 4. Measured water vapor partial pressure dependence of $\text{Al}(\text{OH})_3(\text{g})$ formation from Al_2O_3 at 1450°C .

Typically, some formation of ledges on the (0001) basal plane of the sapphire surface was observed after exposure in water vapor at elevated temperatures. An example of this is shown in Figure 5. The contrast in this FE-SEM micrograph has been enhanced to bring out these features. More distinct surface pitting was observed in coupons that had surface damage due to grit blasting of holes for suspension in the TGA, as shown in Figure 6. More often, holes were machined in the coupons using a diamond core drill. The core-drilled coupons did not show the distinct pitting shown in Figure 6. After observing the geometric pits, the possibility of exposing surface damaged coupons in water vapor to study surface energies and equilibrium faceting of pits was considered. However, the crystallographic orientation of the pits shown in Figure 6 did not correspond to the expected equilibrium shapes [14,15]. It is possible that water vapor selectively removes material from some crystallographic planes.

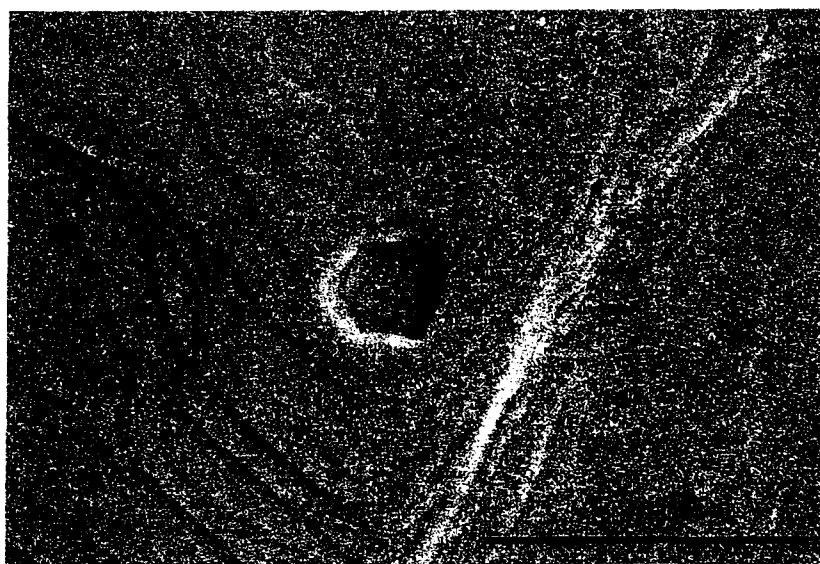


Figure 5. Surface rearrangement of (0001) basal plane of sapphire coupon after exposure at 1250°C , 0.5 atm H_2O /0.5 atm O_2 for 240h.

Having established the magnitude of alumina volatility in water vapor, as well as the pressure and temperature dependence, the durability of alumina in combustion environments can be evaluated next. First, the partial pressures of volatile species in the alumina-water vapor system are compared to those of the silica-water vapor system in Figure 8. These curves were calculated for conditions of 1 atm water vapor using the data of Gurvich et al.[6] for $\text{Al}(\text{OH})_3(\text{g})$, Hashimoto [7] for $\text{Si}(\text{OH})_4(\text{g})$ and Krikorian [16] for $\text{SiO}(\text{OH})_2(\text{g})$. The $\text{SiO}(\text{OH})_2(\text{g})$ species increases in importance for the Si-O-H system at higher temperatures. However, the thermodynamic data for this species are not well known, so the position of this curve is not certain. Nevertheless, this plot shows that in the temperature range of 1000 to 1500°C, volatile hydroxide formation from alumina is one to two orders of magnitude less than from silica.

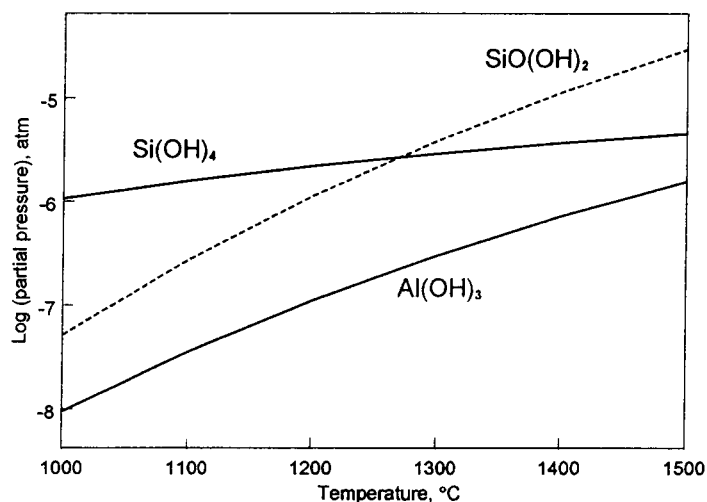


Figure 8. Comparison of silica and alumina volatility in 1 atm water vapor. Calculated using data of Hashimoto [7], Krikorian [16], and Gurvich[6].

Second, for long-term application of alumina-based components, a hypothetical recession criterion of 250 μm in 10,000 h has been chosen and mapped for a gas velocity of 50 m/sec as a function of temperature and pressure, as shown in Figure 9. The lower left hand corner of the map corresponds to low volatility conditions, whereas the upper right corner corresponds to high volatility conditions. Using the data of Gurvich et al. [6] for $\text{Al}(\text{OH})_3(\text{g})$, a specific weight loss of alumina has been calculated for 10,000 hours using Equation 3. The weight loss was then converted to alumina recession using the density of alumina. Typical turbine engines operate at total pressures of about 10 atm. Thus an upper temperature limit for alumina to meet the recession criterion of 250 μm in 10,000h for a gas velocity of 50 m/sec is about 1300°C. A gas velocity of 50 m/sec is typical of the combustor area of a turbine engine. Turbine blades and vanes would see gas velocities on the order of 500 m/sec, and would thus have lower temperature limits for the same recession criterion. This type of map would need to be recalculated for different recession criteria as well as different gas velocities.

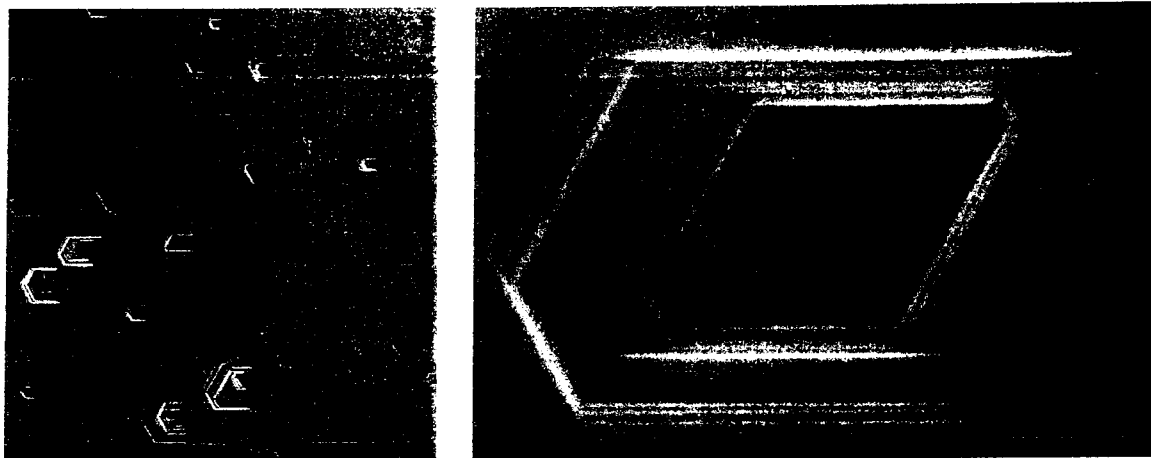


Figure 6. Surface pitting of damaged (0001) basal plane of sapphire coupon after exposure at 1350°C, 0.5 atm H₂O/0.5 atm O₂ for 94h.

Additional surface rearrangement was observed on ground beveled edges of the sapphire coupons exposed in high temperature water vapor, as shown in Figure 7. The distinct geometric features of the coupon after exposure for 72h at 1450°C in 0.68 atm water vapor is compared to the as-received coupon as well as a coupon exposed for 240h at 1500° in oxygen. This comparison demonstrates that the surface rearrangement is due to the high temperature water vapor and is not simply a thermal process.

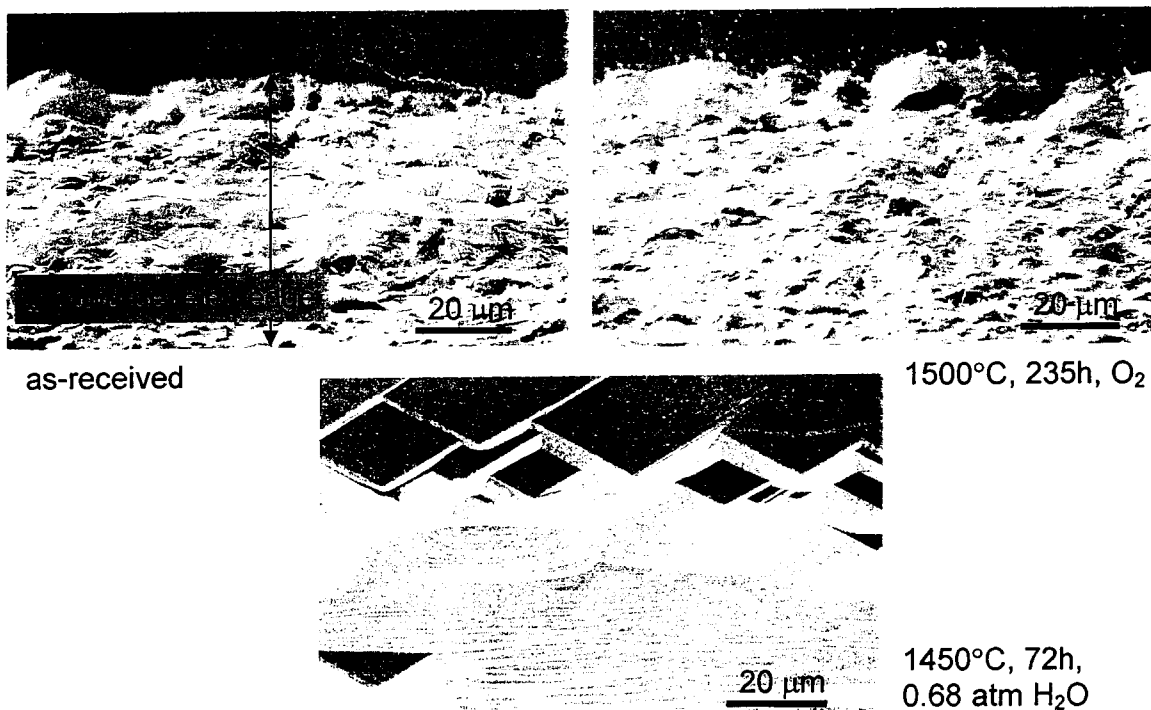


Figure 7. Surface rearrangement of beveled edge of sapphire coupon in high temperature water vapor.

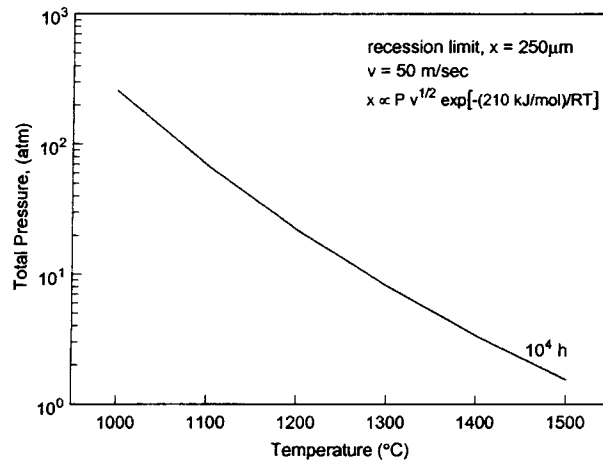


Figure 9. Recession map for alumina at a gas velocity of 50 m/s given a recession limit of 250 μm in 10,000h. Pressure and temperature conditions below the line meet the criterion. Conditions above the line are too severe to meet the allowable recession limit.

SUMMARY AND CONCLUSIONS

Alumina volatility in water vapor was measured by weight loss and found to agree with literature values. The water vapor partial pressure dependence of alumina volatility was consistent with $\text{Al}(\text{OH})_3(\text{g})$ formation. Surface rearrangement of sapphire coupons was observed in high temperature water vapor, consistent with a volatilization process. Recession was found to be proportional to pressure, the square root of gas velocity, and varied exponentially with temperature based on an enthalpy of $\text{Al}(\text{OH})_3(\text{g})$ formation from alumina and water vapor of 210 kJ/mol. Based on volatile hydroxide formation mechanisms alone, alumina-based systems will have longer lifetimes than silica-based systems. Nevertheless, volatility will limit the long-term application of alumina-based systems as structural material temperatures of turbine engines exceed 1300°C.

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